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BRIEF COMMUNICATIONS

Superconducting Properties in the $Li_{1+x}Ti_{2-x}O_4$ System with the Spinel Structure

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The spinel system $Li_{1+x}Ti_{2-x}O_4$ was synthesized by a method differing from earlier ones, and the resistivities in magnetic fields were examined. The system was chemically homogeneous over the composition range $0 \leq x \leq \frac{1}{3}$ and no chemical instabilities were observed. The substitution of the Ti by the Li on the octahedral sites changes the electronic state of neighboring Ti ions from a conducting one to a localized state; consequently, nonconducting domains are produced in the conducting domain clusters. The superconducting properties of the system are discussed in terms of percolation paths through superconducting domains.

Introduction

The spinel compound $LiTi_2O_4$ was found by Johnston *et al.* (*1*) to be a superconductor with a transition temperature $T_c = 11$ K. The solid solution system $Li_{1+x}Ti_{2-x}O_4$ ($0 \leq x \leq \frac{1}{3}$) was also investigated (*2–6*) with regard to the compositional dependence of the electronic properties such as the normal superconducting or metallic-semiconducting transition. The results are summarized as follows: (1) The system transforms from a metallic to semiconducting phase near $x \simeq 0.1$, (2) T_c is almost independent on the composition x, (3) the superconducting fraction decreases with increasing x. The critical composition is about $x = 0.16$.

The spinel system $Li_{1+x}Ti_{2-x}O_4$ was initially reported by Deschanvres *et al.* (*7*) to form a complete solid solution over the composition range $0 \leq x \leq \frac{1}{3}$. Later, Johnston and co-workers (*2–4*) reported difficulties with the preparation of the solid solution and were unable to resolve the character of the metal-semiconductor transition, because of chemical instabilities associated with a deviation from Vegard's law (see Fig. 1) that peaked near $x \simeq 0.1$. Subsequently, Harrison *et al.* (*6*) reported that the instabilities are due to a disproportionation into Li-rich and Li-poor compositions at the grain boundaries. They also claimed that the superconductivity of the solid solutions is due to the stoichiometric

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$LiTi_2O_4$ which was produced by the spinodal decomposition but remained undetected by X-ray diffraction.

The high T_c oxide superconductors such as $(La,Ba)_2CuO_{4-\delta}$ and $YBa_2Cu_3O_y$, which have recently attracted the interest of many researchers, also show a wide range of solid solution or nonstoichiometry. The purpose of this study is to clarify whether the transport properties of the solid solution system $Li_{1+x}Ti_{2-x}O_4$ are due to coexisting $LiTi_2O_4$ or to intrinsic properties of the solid solutions.

Experimental and Results

Sample Preparation

We synthesized powder samples using techniques which differed from earlier methods (*1*, *5–7*). $Li[Li_{1/3}Ti_{5/3}]O_4$ was, as a first step, synthesized by solid-state reaction of lithium carbonate (4N), titanium dioxide (4N), and titanium metal (3N). The mixture was pelletized, preheated in air for 1 day at 600°C, fired for 1 day at 950°C, and then ground and reheated for 2 days at 900°C. Additional Li_2CO_3 (about 0.9 mole%) was needed to obtain a single phase, because of the volatilization of low melting Li_2O produced by the decomposition of Li_2CO_3. Subsequently, $Li_{1+x}Ti_{2-x}O_4$ was prepared by heating pelletized mixtures of $Li_{4/3}Ti_{5/3}O_4$, TiO_2, and Ti metal powder in an evacuated silica tube at 760°C for 1 week. Phase identification was carried out by an X-ray powder diffraction with monochromatic Cu*Kα* radiation. The lattice parameter was determined by the least-squares method. The samples crystallize in the spinel structure in the composition range $0 \leq x \leq \frac{1}{3}$; no second phase was recognized. Figure 1 shows the x-dependence of the lattice parameter (a) for $Li_{1+x}Ti_{2-x}O_4$, where the content of Li is the nominal compositions. The lattice parameter for $LiTi_2O_4$ agrees with those reported previously (*2*, *6*). It decreases linearly with increasing x; the compositional dependence obeys Vegard's law observed in the "stable" samples of Harrison *et al.* (*6*), as shown in Fig. 1. In this study no deviations from Vegard's law were observed near $x \simeq 0.1$ and no chemical instabilities were found. In fact, the samples were stable when they were exposed to the air for several days. These discrepancies relative to the findings of Refs. (*2–4*) and (*6*) may derive from differences in the method of sample preparation.

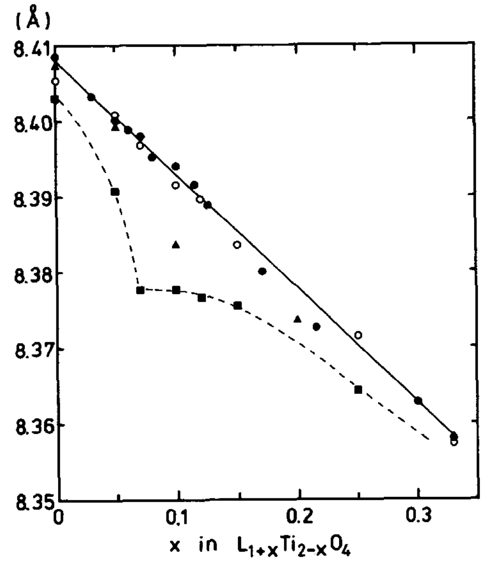

FIG. 1. Lattice parameter (a) vs composition x for $Li_{1+x}Ti_{2-x}O_4$. ●, Present data; ▲, Johnston (Ref. (*2*)), ○ ("stable") and ■ ("unstable"), Harrison *et al.* (Ref. (*6*)).

Resistivity and Ac Susceptibility

Resistivities of samples with various x values were measured in magnetic fields by a standard four probe method, with a current of 1 mA. At zero magnetic field, the onset temperatures of superconducting transition are roughly 12 K, independent of composition x; the transition width increases with increasing x above $x \simeq 0.08$. The sample with $x = 0.12_5$ does not show

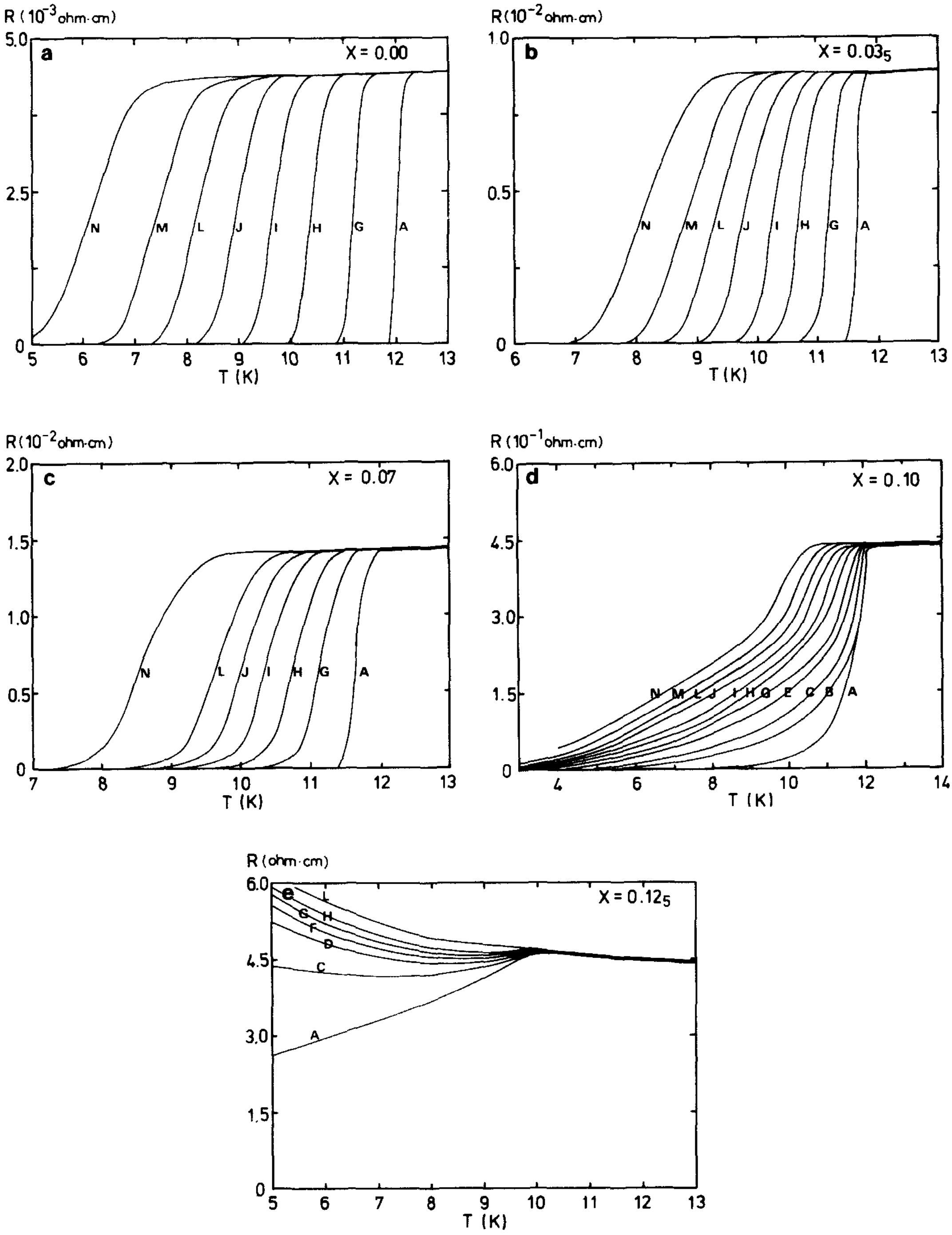

FIG. 2. Temperature (T) dependence of resistivity (R) for samples with $x = 0.00$, 0.03_5, 0.07, 0.10, and 0.12_5 in magnetic fields (A, 0; B, 0.3; C, 1; D, 3; E, 5; F, 6; G, 10; H, 20; I, 30; J, 40; L, 50; M, 60; and N, 75 kOe).

zero-resistivity at 4.2 K. The resistivities of the normal conducting state continuously increase with increasing x from about 5×10^{-3} ohm cm for $x = 0$ to 5 ohm cm for $x = 0.12_5$.

The magnetic field dependences of the resistivities differ among samples with various x values. Typical results are shown in Fig. 2. For samples with $x = 0.00$, 0.03_5, and 0.07, T_c continuously decreases with increasing magnetic fields, showing a sharp transition. In samples with $x = 0.10$ and 0.12_5, on the other hand, the transition is broad and the resistivity (R) vs temperature (T) curves show a "tail" below T_c which becomes more pronounced with increasing magnetic fields and x. The resistivity for $x = 0.12_5$ shows semiconductive behavior above 1 kOe.

In Fig. 3, Hc_2–T_c curves for samples with $x = 0.00, 0.03_5, 0.07$, and 0.10 are plotted as a function of temperature. The coherence length $\xi(T)$ calculated from the estimate of $Hc_2(T)$ defined at 90% of the normal state resistivity obeys the Ginzburg–Landau relation for dirty limit superconductors.

$$\xi(T) = 0.852(\xi_0 l)^{1/2} \cdot (1 - T/T_c)^{-1/2}.$$

In Table I, $\xi_0 l$, as estimated from the extrapolation to $T = 0$, is shown with $Hc_2(0)$, derived from the Helfand–Werthamer theory (*8*), and $-(dHc_2/dT)_{T_c}$ is used for the calculation. It is noted that $Hc_2(0)$ increases with increasing x.

Figure 4 shows the compositional dependence of superconducting volume fractions obtained from *ac* susceptibility measurements (the inset in Fig. 4). The superconducting fraction decreases with increasing x, in agreement with data by Harrison *et al.* (*6*). The critical composition is roughly $x = 0.15$.

Discussion

The average charge of Ti ions is +3.5 in $LiTi_2O_4$ and the t_{2g}(Ti) conduction band is partially occupied (5, 6, 9). In $Li_{1+x}Ti_{2-x}O_4$, when Li ions are randomly substituted for Ti ions on the octahedral sites, the average charge of Ti should increase and finally reach +4 in $Li_{4/3}Ti_{5/3}O_4$, at which point the conduction band is empty. Thus the metal–insulator (semiconductor) transition should occur at an intermediate composition. As mentioned above, the resistivity of the normal conducting state continuously increases with increasing x and begins to show a semiconducting behavior above $x \simeq 0.12$.

In this study, no deviation from Vegard's law was observed over the composition range $(0 \leq x \leq \frac{1}{3})$ in $Li_{1+x}Ti_{2-x}O_4$. If spinodal decomposition had occurred on a microscopic scale, as postulated in Ref. (*6*), one would observe broadening of the X-ray diffraction peaks or satellite peaks, corresponding to the scale of texture. However, the X-ray diffraction peaks were very sharp, and no satellite peaks or second phases were recognized in this study. We believe that the solid solution system $Li_{1+x}Ti_{2-x}O_4$ is chemically homogeneous, i.e., that the additional Li ions are randomly distributed on octahedral sites. This is also supported by the facts that the upper critical field shows the compositional dependence shown in Table I and that the magnetic field dependences of the resistivities differ in the range $0 \leq x \leq 0.08$ and $x \geq 0.08$. If the superconducting properties of

TABLE I

MEASURED PARAMETERS FOR $Li_{1+x}Ti_{2-x}O_4$

x:	0.00[a]	0.03_5	0.07	0.10
$\xi_0 l$ (Å)	2134	1429	1256	944
$-(Hc_2/dT)_{T_c}$ (kOe/K)	15.3	26.2	30.3	44.7
$Hc_2(0)$ (kOe)	129	214	248	369

[a] The lower critical field Hc_1 and Hc (thermodynamical critical field) at 4.2 K are about 700 Oe and 3.8 kOe, respectively.

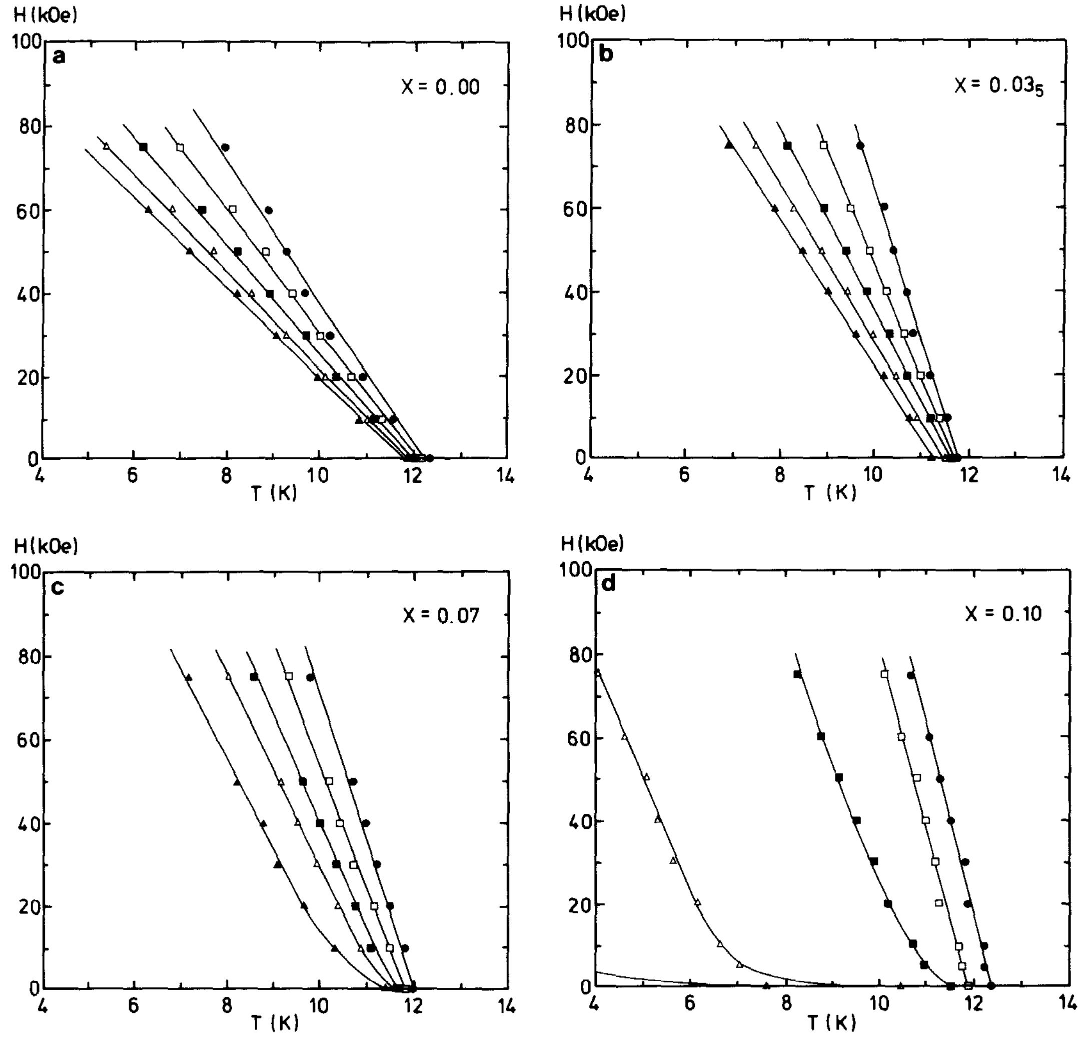

FIG. 3. Upper critical field (Hc$_2$)–Temperature (T) curves for samples with x = 0.00, 0.03$_5$, 0.07, and 0.10. ●, Onset; □, $R = 0.9R_n$; ■, $R = 0.5R_n$; △, $R = 0.1R_n$; and ▲, $R = 0$ (R_n, resistivity of normal conducting state).

Li$_{1+x}$Ti$_{2-x}$O$_4$ were due to LiTi$_2$O$_4$ deposited on the grain boundaries, as was asserted in Ref. (*6*), those would remain unchanged over the composition range. Recently, ^{7}Li NMR study was performed on the superconducting Li$_{1+x}$Ti$_{2-x}$O$_4$ (*10*), which showed that these metallic spinel compounds are chemically homogeneous bulk superconductors.

In the spinel structure of LiTi$_2$O$_4$, eight molecules of LiTi$_2$O$_4$ are contained in a unit cell. At $x = 0.125$, close to the critical composition $x = 0.15$, 1 of 16 octahedral Ti atoms per unit cell has been replaced by Li. Therefore, we assume that when the unit cell contains more than one Li ion on octahedral site the superconducting path is interrupted. If the Ti ions on the octahedral

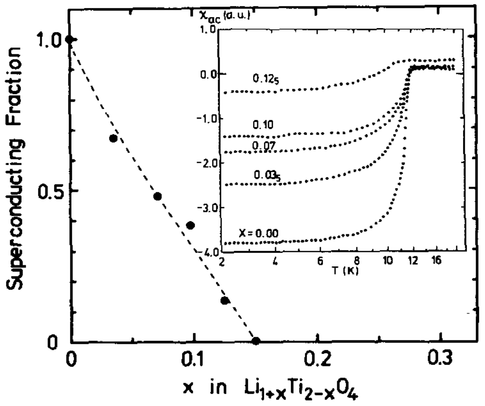

FIG. 4. Superconducting volume fraction vs composition x in $Li_{1+x}Ti_{2-x}O_4$. The inset shows *ac* susceptibilities of samples with $x = 0.00$, 0.03_5, 0.07, 0.10, and 0.12_5.

sites were ideally substituted for by the Li, this model would give a percolation limit $x \simeq 0.09$, for the superconducting path. By "ideally," we mean that no more than one Ti ion per unit cell is replaced by Li until one Ti ion per unit cell has been replaced. Below $x \simeq 0.09$, the superconducting paths are linked together and superconducting transition in R–T curves is sharp in magnetic fields. Near the percolation limit the superconducting domains may be linked by coupling between the superconducting domains and the resistivity falls to zero. Under magnetic fields, the coupling breaks down in increasing magnetic fields and the resistivity below T_c begins to show the "tail."

Such features are also supported by the NMR study (*10*). The ^7Li nuclear relaxation rate $1/T_1$ of $Li_{1+x}Ti_{2-x}O_4$ is composed of two relaxation processes, the Korringa process due to the conduction electrons and one due to the magnetic relaxation centers. The former is almost independent of x but the latter increases with increasing x, indicating an increase in the number of the magnetic relaxation centers. The increase in magnetic centers with increasing x was also confirmed by the analysis of magnetic susceptibility and ESR study (*5, 6*). Thus, the substitution of Ti ions on the octahedral sites by Li changes the neighboring Ti ions from a conducting one to a localized state. Nonconducting domains are produced in the conducting domain clusters and cut the superconducting path.

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